HIGH-FIELD HIGH-FREQUENCY EPR STUDIES ON METAL-METAL INTERACTIONS IN BINUCLEAR OXYGEN-BRIDGED IRON(III) COMPOUNDS

A. Ozarowski (NHMFL)

Introduction

Strong antiferromagnetic exchange interactions between two high-spin Iron(III) ions in the title compounds give rise to the spin states of the binuclear system that are characterized by the total spin quantum numbers \( S \) ranging from 0 to 5 with the singlet state \( (S=0) \) being the ground state. \(^1\text{-}^3\) Higher spin states, triplet, \( S=1 \), quintet, \( S=2 \) and septet, \( S=3 \), are thermally accessible at the room temperature. EPR studies on such compounds are extremely rare. \(^1\text{-}^3\)

Experimental

We report here the measurements performed on the 15/17 Tesla instrument at the frequencies between 95 and 380 GHz on two isomeric compounds with a formula \([\text{Fe(phen)}]_2\text{O(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}\) where phen is 1,10-phenanthroline. The sensitivity of the high-frequency instrument that employs no resonance cavity was sufficient for recording spectra due to both the triplet states and the weakly populated quintet states (the latter appears as a group of strong lines around 7.9 T in Fig. 1).

Results and Discussion

Table 1: Spin Hamiltonian parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>( g_x ), ( g_y ), ( g_z )</th>
<th>( D ) (cm(^{-1}))</th>
<th>( E ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>green ([\text{Fe(phen)}]_2\text{O(SO}_4\text{)}_2\cdot6\text{H}_2\text{O})</td>
<td>2.010, 2.008, 2.015</td>
<td>4.15</td>
<td>0.677</td>
</tr>
<tr>
<td>orange ([\text{Fe(phen)}]_2\text{O(SO}_4\text{)}_2\cdot6\text{H}_2\text{O})</td>
<td>2.012, 2.012, 2.00</td>
<td>4.86</td>
<td>0.262</td>
</tr>
</tbody>
</table>

The spin Hamiltonian parameters for \( S=1 \) were determined for each of complex (Table 1). The magnitudes of the \( D \) and \( E \) parameters indicate that the low-frequency EPR is clearly not suitable to study the triplet states in this important class of compounds. The work on interpretation of the \( S=2 \) state spectrum is still in progress.

Conclusions

(1) Triplet state EPR spectra in binuclear iron (III) complexes can be observed at very high frequencies and very high magnetic fields. (2) Anisotropic metal-metal exchange interactions must contribute to the zero-field splitting. (3) Assumption of the isotropic \( g = 2 \) that is satisfactory in X or Q Band must be abandoned in high-field EPR.

Acknowledgements

This work was supported by NHMFL through project 7300-042. NHMFL is funded by the NSF through Grant DMR-0084173 and the state of Florida.

References